

Heteroleptic diphenylamido complexes of ytterbium: syntheses and molecular structures of $(\text{MeC}_5\text{H}_4)_2\text{YbNPh}_2(\text{THF})$ and $(\text{C}_5\text{Me}_5)_2\text{YbNPh}_2$

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Abstract

Reaction of ytterbocene chloride with NaNPh_2 in THF or toluene–THF at 0°C yielded the neutral diphenylamido complexes $(\text{MeC}_5\text{H}_4)_2\text{YbNPh}_2(\text{THF})$ (**1**), $(t\text{-BuC}_5\text{H}_4)_2\text{YbNPh}_2(\text{THF})$ (**2**) and $(\text{C}_5\text{Me}_5)_2\text{YbNPh}_2$ (**3**) in good yields. The crystal structures of **1** and **3** were identified by X-ray diffraction analysis. Complex **1** has a distorted tetrahedral arrangement around ytterbium by two MeC_5H_4 groups, one oxygen atom and one nitrogen atom [orthorhombic, space group *Pbca* (no. 61); $a = 15.188(1)$, $b = 18.145(1)$, $c = 17.444(1)$ Å; $V = 4807.3(5)$ Å³, $Z = 8$, $D_{\text{calc.}} = 1.579$ g cm⁻³]. The crystal structure of **3** [monoclinic, space group *P2₁/n*; $a = 15.834(2)$, $b = 9.992(2)$, $c = 18.504(3)$ Å; $\beta = 104.060(10)^\circ$, $V = 2839.9(8)$ Å³, $Z = 4$, $D_{\text{calc.}} = 1.431$ g cm⁻³] shows a triangular array of two C_5Me_5 groups and one nitrogen atom surrounding ytterbium with additional intramolecular Yb–η²-Ph chelate interactions [Yb–C = 2.986(6) and 3.053(6) Å]. The complexes **1** and **2** exhibit good catalytic activity for the polymerization of methyl methacrylate. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Synthesis; X-ray structure; Ytterbocene amides; Diphenylamide complex

1. Introduction

In the last two decades, organolanthanide amides have attracted much attention. This might be for the two following reasons. First, anionic amides are the suitable alternated ancillary ligands to replace the cyclopentadienyl group usually used. Secondly, lanthanocene amides have been found to be the catalysts or precatalysts for important homogeneous processes, such as hydroamination/cyclization of aminoalkenes [1], and polymerization of methyl methacrylate [2] and ε-caprolactone [3]. During our study on the chemistry of organolanthanide amides, we found that diisopropylamido bis(methylcyclopentadienyl) lanthanides $(\text{MeC}_5\text{H}_4)_2\text{LnN}(i\text{-Pr})_2(\text{THF})$ and piperidino bis(methylcyclopentadienyl) lanthanides $(\text{MeC}_5\text{H}_4)_2\text{LnNC}_5\text{H}_{10}$

$\text{HNC}_5\text{H}_{10}$ are highly effective initiators for the polymerization of methyl methacrylate [4,5] and phenyl isocyanate [6]. Besides, they all show good catalytic activity for ring-opening polymerization of ε-caprolactone [7]. These interesting results prompted us to investigate further the effect of amido ligands and π-ligands around central metals on the catalytic behavior. Here we report the synthesis of ytterbocene diphenylamide complexes, molecular structures and their catalytic behavior for the polymerization of methyl methacrylate.

2. Results and discussion

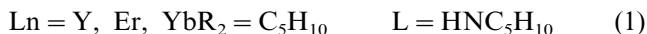
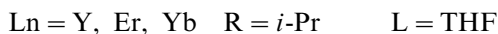
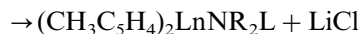
2.1. Synthesis

The metathetical reaction of lanthanocene chloride with alkali metal amides is a popular method for the synthesis of organolanthanide amides [8]. For example, the neutral lanthanocene amide complexes $(\text{MeC}_5\text{H}_4)_2\text{-}$

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$\text{LnN}(i\text{-Pr})_2(\text{THF})$ [6], $(\text{MeC}_5\text{H}_4)_2\text{LnNC}_5\text{H}_{10}(\text{HNC}_5\text{H}_{10})$ [5] were reported to be synthesized by the reaction of lanthanocene chloride with corresponding lithium amides (Eq. (1)).



However, the reaction with lithium diphenylamide gives anionic complexes containing lithium salt $[\text{Li}(\text{DME})_3][\text{CH}_3\text{C}_5\text{H}_4\text{Ln}(\text{NPh}_2)_3]$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) [9], $[\text{Li}(\text{DME})_3][(\text{C}_5\text{H}_5)_2\text{Nd}(\text{NPh}_2)_2]$ [10], which have ion-pair structure. Schumann et al. also isolated the anionic

Table 1

Selected bond distances (Å) and angles (°) for complex **1**

Bond distances			
Yb–N	2.286(7)	Yb–O	2.329(6)
Yb–C13	2.642(9)	Yb–C14	2.601(10)
Yb–C15	2.576(10)	Yb–C16	2.613(9)
Yb–C17	2.641(10)	Yb–C19	2.662(11)
Yb–C20	2.640(9)	Yb–C21	2.609(9)
Yb–C22	2.639(10)	Yb–C23	2.623(10)
Yb–Cent(1) ^a	2.331	Yb–Cent(2) ^b	2.354
Bond angles			
N–Yb–O	93.6(2)	N–Yb–Cent(1)	111.4
N–Yb–Cent(2)	111.9	O–Yb–Cent(1)	105.1
O–Yb–Cent(2)	102.8	Cent(1)–Yb–Cent(2)	126.0
C1–N–C7	115.1(6)	C1–N–Yb	128.0(5)
C7–N–Yb	116.3(4)		

^a Cent(1) is the centroid of the C(13)–C(17) ring.

^b Cent(2) is the centroid of the C(19)–C(23) ring.

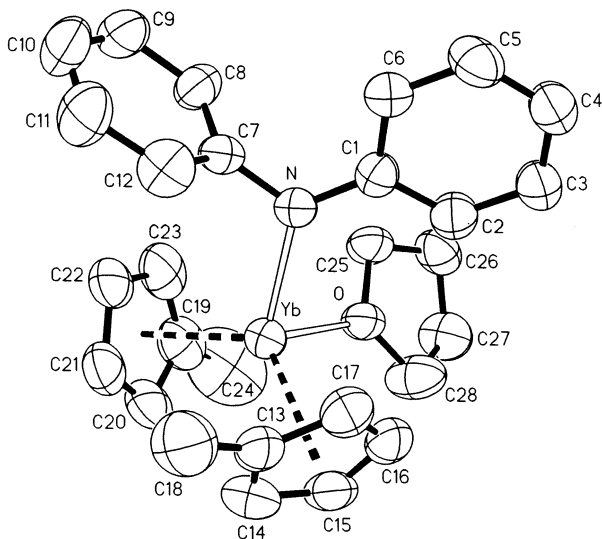


Fig. 1. Molecular structure of complex $(\text{MeC}_5\text{H}_4)_2\text{YbNPh}_2(\text{THF})$ (**1**) with atomic numbering (hydrogen atoms have been omitted for clarity).

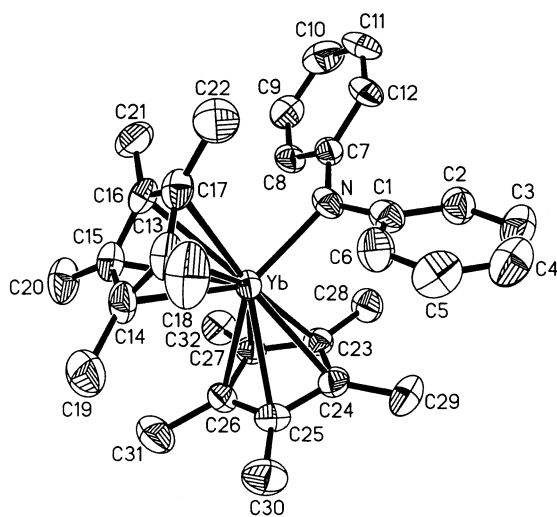
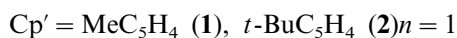
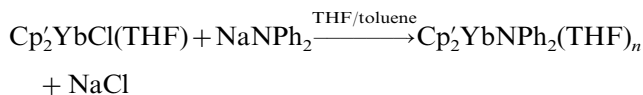


Fig. 2. Molecular structure of complex $(\text{C}_5\text{Me}_5)_2\text{YbNPh}_2$ (**3**) with atomic numbering (hydrogen atoms have been omitted for clarity).

complex $[\text{Li}(\text{THF})_4][(\text{C}_5\text{H}_5)_2\text{Ln}(\text{NPh}_2)_2]$ ($\text{Ln} = \text{Lu}, \text{Sm}$) from the reaction of methyl-bridged organolanthanide alkyl $(\text{C}_5\text{H}_5)_2\text{Ln}(\mu\text{-Me})_2\text{Li}(\text{tmed})$ with diphenylamine [11]. It was reported that alkali metals often induced structural changes in organolanthanide complexes [8c,12]. We attempt to use NaNPh_2 instead of LiNPh_2 as a reagent to synthesize the neutral diphenylamido complexes.

According to expectation, the reaction of lanthanocene chloride with sodium diphenylamide gives the desired heteroleptic amide complexes in good yields. No matter whether the π -ligands are methylcyclopentadienyl, *tert*-butylcyclopentadienyl or pentamethylcyclopentadienyl groups, the products are all free of sodium salt as shown in Eq. (2).



All these complexes are extremely sensitive to air and moisture. Complexes **1** and **2** are highly soluble in THF and DMF, moderately in diethyl ether and aromatic solvents, and insoluble in aliphatic hydrocarbons. Complex **3** has good solubility even in aliphatic hydrocarbons such as pentane, hexane etc.

2.2. X-ray crystal structures of **1** and **3**

Complexes **1** and **3** were characterized by X-ray diffraction to be monomers. The molecular structures are shown in Figs. 1 and 2 and the important bond lengths and angles are listed in Tables 1 and 2, respectively.

Complex **1** is a THF-solvated complex as shown in Fig. 1. The ytterbium metal is coordinated by two

Table 2
Selected bond distances (Å) and angles (°) for complex **3**

<i>Bond distances</i>			
Yb–N	2.216(5)	Yb–C13	2.605(6)
Yb–C14	2.619(6)	Yb–C15	2.609(6)
Yb–C16	2.601(6)	Yb–C17	2.619(6)
Yb–C23	2.593(6)	Yb–C24	2.607(6)
Yb–C25	2.607(6)	Yb–C26	2.612(6)
Yb–C27	2.578(6)	Yb–C1	2.986(6)
Yb–C6	3.053(6)	Yb–Cent(1) ^a	2.318
Yb–Cent(2) ^b	2.306		
<i>Bond angles</i>			
N–Yb–Cent(1)	109.8	N–Yb–Cent(2)	110.6
Cent(1)–Yb–Cent(2)	138.5	C1–N–C7	120.9(5)
C1–N–Yb	109.6(4)	C7–N–Yb	128.9(4)
N–C1–C6	117.3(6)		

^a Cent(1) is the centroid of the C(13)–C(17) ring.

^b Cent(2) is the centroid of the C(23)–C(27) ring.

MeC₅H₄ rings, one oxygen atom of THF and one nitrogen atom from the diphenylamido group to form a distorted tetrahedral geometry, giving the central metal a formal coordination number of eight. The bond angles Cent(1)–Yb–Cent(2) 126.0° and N–Yb–O 93.6(2)° are in good agreement with the corresponding values Cent(1)–Er–Cent(2) 126.3° and N(1)–Er–N(2) 93.0(2)° in (MeC₅H₄)₂ErNC₅H₁₀(HNC₅H₁₀) [5]. The two methyl groups in the cyclopentadienyl rings are located at opposite sides. Similar *trans* orientations have been observed in (MeC₅H₄)₂ErNC₅H₁₀(HNC₅H₁₀), [(MeC₅H₄)₂YbCl]₂ [13] and [(MeC₅H₄)₂Yb(THF)₂][BPh₄] [14].

The metrical parameters in **1** are unexceptional. The Yb–O (THF) distance in **1**, 2.329(6) Å, is similar to the Yb–O (THF) distances in (*t*-BuC₅H₄)₂YbCl(THF), 2.333(6) Å [15] and (C₅Me₅)₂YbCl(THF), 2.362 Å [16]. The Yb–C(ring) distances range from 2.576(10) to 2.662(11) Å. The Yb–C(ring) average distance of 2.625 Å is in the range of values found in other ytterbocene complexes: [(MeC₅H₄)₂YbCl]₂, 2.585 Å [13]; [(C₅H₅)₂YbCl]₂, 2.58 Å [17]; (*t*-BuC₅H₄)₂YbCl(THF), 2.628 Å; (C₅Me₅)₂YbCl(THF), 2.65 Å.

The Yb–N bond distance (2.286(7) Å) compares well with the distances found in other lanthanocene amide complexes: [(MeC₅H₄)₂Yb(μ-NH₂)]₂, 2.31 Å [18]; (C₅H₅)₂Lu(NC₄H₂Me₂)(THF), 2.289(4) Å [8d]; [Li(THF)₄][(C₅H₅)₂Lu(NPh₂)₂], 2.290(7), 2.293(7) Å [11]; [Li(DME)₃][(C₅H₅)₂Nd(NPh₂)₂], 2.421(7), 2.434(7) Å [10] when corrections are made for trivalent eight-coordinate ionic radii [19]. However, the Yb–N bond distance is larger than those found in (MeC₅H₄)₂ErNC₅H₁₀(HNC₅H₁₀) (2.159(8) Å) [5], (C₅Me₅)₂La–NHCH₃(NH₂CH₃) (2.313(10) Å) [20], even if the differences between Yb and La, Yb and Er in radii are considered.

Complex **3** is an unsolvated complex (Fig. 2). The ytterbium atom is coordinated by two C₅Me₅ rings and

one nitrogen from diphenylamido group to form a near-triangular arrangement. There is an additional intramolecular Yb–η²-Ph interaction, due to π-bonding of the phenyl group. Thus, the coordinated geometry around ytterbium atom may be described to be a distorted tetragonal pyramidal array composed of two C₅Me₅ ring centroids, N, C(1) and C(6). The bond angles C(7)–N–Yb and C(1)–N–Yb are 128.9(4) and 109.6(4)°, respectively. The difference of the two bond angles (19.3°) is significantly larger than that of **1** (11.7°), which might result from the presence of the chelate interaction. The bond distances of Yb–C(1) and Yb–C(6) are in the range of η-Ph–Ln bonding values published. The lengths 2.986(6) and 3.053(6) Å for Yb–C(1) and Yb–C(6), respectively are similar to 2.739(35)–3.010(48) Å in Yb(η⁶-C₆Me₆)(AlCl₄)₃-MeC₆H₅ [21], 2.986(6), 3.180(9) Å for bridging η²-C₅H₅ bonding in (C₅Me₅)₂Sm(μ-C₅H₅)Sm(C₅Me₅)₂ [22] and 2.814(4)–3.148(6) and 2.946(6)–3.158(9) Å for chelating η⁶-, η¹-Ph–Ln bonding in [Yb(Odpp)₃] (Odpp[−] = 2,6-diphenylphenolate) [23] and in Nd(Odpp)₃ [24], respectively. To our best knowledge, this is the first example of organolanthanide amide complexes with intramolecular Yb–η²-Ph chelate interactions. The Yb–C(ring) distances range from 2.578(6) to 2.619(6) Å. The Yb–C(ring) average distance of 2.605 Å is slightly shorter than 2.750(15) Å Sm–C(ring) average distance in (C₅Me₅)₂SmN(SiMe₃)₂ [25] and 2.682(4), 2.678(4) Å Y–C(ring) distances for the two independent molecules in (C₅Me₅)₂YN(SiMe₃)₂ [26], even if subtraction of the differences in ionic radii was carried out [19]. The Yb–N bond length 2.216(5) Å is comparable to that in **1** and similar to the 2.301(3) Å Sm–N distance in (C₅Me₅)₂SmN(SiMe₃)₂ and 2.274(5), 2.253(5) Å Y–N distances in (C₅Me₅)₂YN(SiMe₃)₂. The bond angle Cent(1)–Yb–Cent(2) of 138.5° is larger than 132.2 and 132.4° in (C₅Me₅)₂YN(SiMe₃)₂ and 132.8° in (C₅Me₅)₂SmN(SiMe₃)₂, which reflects the smaller size of NPh₂ ligand set in **3**.

2.3. Catalytic activity

We tested the catalytic activity of complexes **1**, **2** and **3** for the polymerization of methyl methacrylate and the preliminary results show that complexes **1** and **2** have good catalytic activity. They give a conversion as high as 95% for **1** and 100% for **2** at 0°C for 2 h in the case of 0.2 mol% catalyst concentrations. The number-average molecular weights and the molecular weight distributions are 253 × 10³, 133 × 10³ and 1.67, 1.26, respectively. The polymerization reaction can proceed at a wide range of temperature from −40 to 40°C. However, complex **3** has no activity at all under the same polymerization conditions. This may be because the two bulky pentamethylcyclopentadienyl groups and amido group (NPh₂) sterically crowd around the central

ytterbium and make it difficult to initiate the insertion of methyl methacrylate (MMA). Further study is in progress on the relationship between the size of ligands around the central metal and the polymerization activity.

3. Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Toluene, THF and diethyl ether were dried over Na or sodium benzophenone ketyl and distilled before use. MMA was dried over calcium hydride powder for 4 days and stored over 3 Å molecular sieves under argon after distillation. NaNPh_2 was prepared as reported in the literature [27].

Melting points were determined in a sealed argon-filled capillary and uncorrected. Lanthanide metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion. The IR spectra were obtained as KBr pellets on a Magna-550 spectrometer.

3.1. Preparation of $(\text{MeC}_5\text{H}_4)_2\text{YbNPh}_2(\text{THF})$ (**1**)

To a solution of $(\text{MeC}_5\text{H}_4)_2\text{YbCl}$ [6] in THF (51.3 ml, 8.82 mmol) was added 15.8 ml of a THF solution of NaNPh_2 (8.82 mmol). The mixture was stirred for 1 h at 0°C and then for another 48 h at room temperature. After complete removal of THF, the residue was extracted with diethyl ether to remove NaCl. The extracts were concentrated and cooled to -30°C for crystallization. Dark red crystals were formed. Yield: 3.83 g (76%). Single crystals suitable for X-ray diffraction studies were obtained by recrystallization of **1** from diethyl ether–toluene. m.p. = $123\text{--}126^\circ\text{C}$. Anal. Calc. for $\text{C}_{28}\text{H}_{32}\text{NOYb}$: C, 58.84; H, 5.64; N, 2.45; Yb, 30.27. Found: C, 58.22; H, 5.36; N, 2.41; Yb, 30.53%. IR (KBr pellet, cm^{-1}): 3042 m, 2970 w, 2919 w, 2873 w, 1593 s, 1508 s, 1495 s, 1455 w, 1419 m, 1311 s, 1245 m, 1173 m, 1030 m, 881 m, 748 s, 692 s.

3.2. Preparation of $(t\text{-BuC}_5\text{H}_4)_2\text{YbNPh}_2(\text{THF})$ (**2**)

This complex was prepared from the reaction of $(t\text{-BuC}_5\text{H}_4)_2\text{YbCl}(\text{THF})$ [15] in toluene (50 ml, 5.62 mmol) with NaNPh_2 in THF (10.1 ml, 5.62 mmol) using a similar procedure to that described above. Dark blue crystals were obtained. Yield: 2.08 g (56.4%). m.p. = $124\text{--}128^\circ\text{C}$. Anal. Calc. for $\text{C}_{34}\text{H}_{44}\text{NOYb}$: C, 62.28; H, 6.76; N, 2.14; Yb, 26.38. Found: C, 61.79; H, 6.67; N, 2.07; Yb, 25.93%. IR (KBr pellet, cm^{-1}): 3080 w, 2963 s, 2910 w, 2870 w, 1593 s, 1506 m, 1497 s, 1462 w, 1365 w, 1312 m, 1219 s, 1157 s, 1026 w, 922 w, 748 s, 691 m, 629 m, 505 s.

3.3. Preparation of $(\text{C}_5\text{Me}_5)_2\text{YbNPh}_2$ (**3**)

To a solution of $(\text{C}_5\text{Me}_5)_2\text{YbCl}(\text{THF})$ [8c] in toluene (53.5 ml, 4.37 mmol) was added to 7.8 ml of a THF solution of NaNPh_2 (4.37 mmol). The mixture was stirred for 1 h at 0°C and then for another 48 h at room temperature. After centrifugation, the solvent was completely removed and the oily residue was extracted with hexane. The extracts were concentrated to about 5 ml and cooled to -30°C for crystallization. Purple crystals were isolated. Yield: 1.96 g (73.3%). m.p. = $168\text{--}174^\circ\text{C}$. Anal. Calc. for $\text{C}_{32}\text{H}_{40}\text{NYb}$: C, 62.84; H, 6.59; N, 2.29; Yb, 28.28. Found: C, 62.45; H, 6.70; N, 2.35; Yb, 27.80%. IR (KBr pellet, cm^{-1}): 3048 w, 2967 m, 2920 s, 2855 m, 1636 m, 1593 s, 1508 s, 1443 w, 1377 w, 1312 s, 1084 m, 876 w, 748 s, 694 m.

Table 3

Experimental data for the X-ray diffraction study of complexes **1** and **3**

	1	3
Formula	$\text{C}_{28}\text{H}_{32}\text{NOYb}$	$\text{C}_{32}\text{H}_{40}\text{NYb}$
Formula weight	571.59	611.69
Temperature (K)	293(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$Pbca$ (no. 61)	$P2_1/n$
<i>a</i> (Å)	15.188(1)	15.834(2)
<i>b</i> (Å)	18.145(1)	9.992(2)
<i>c</i> (Å)	17.444(1)	18.504(3)
β (°)	90	104.060(10)
<i>V</i> (Å ³)	4807.3(5)	2839.9(8)
<i>Z</i>	8	4
<i>D</i> _{calc.} (Mg m ^{−3})	1.579	1.431
Absorption coefficient (mm ^{−1})	3.910	3.312
<i>F</i> (000)	2280	1236
Crystal size (mm)	0.60 × 0.55 × 0.40	0.60 × 0.40 × 0.16
θ range for data collection (°)	2.10–25.59	2.33–25.00
Limiting indices	$-18 \leq h \leq 18,$ $-21 \leq k \leq 21,$ $0 \leq l \leq 19$	$0 \leq h \leq 18,$ $-1 \leq k \leq 11,$ $-22 \leq l \leq 21$
Reflections collected	13 199	6367
Independent reflections (<i>R</i> _{int} = 0.1551)	4164	4672 (<i>R</i> _{int} = 0.0190)
Maximum and minimum transmission	1.348 and 0.511	0.6193 and 0.2412
Data/restraints/parameters	4164/139/281	4672/0/318
Goodness-of-fit on <i>F</i> ²	1.188	0.892
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0718	<i>R</i> ₁ = 0.0338
<i>R</i> indices (all data)	<i>wR</i> ₂ = 0.1697 <i>R</i> ₁ = 0.0813 <i>wR</i> ₂ = 0.1775	<i>wR</i> ₂ = 0.0753 <i>R</i> ₁ = 0.0508 <i>wR</i> ₂ = 0.0792
(Δ/σ) _{max}	0.001	0.001
Largest difference peak and hole (e Å ^{−3})	0.983 and −0.969	1.580 and −0.978

3.4. Polymerization of methyl methacrylate

To a toluene solution (10 ml) of MMA (1 ml, 9.35 mmol) was added at once the toluene solution (1 ml) of (MeCp)₂YbNPh₂(THF) (10.7 mg, 0.019 mmol) with vigorous magnetic stirring at the desired temperature. The polymer was precipitated by ethanol after the polymerization was held for 2 h and then washed with ethanol and dried in vacuum.

3.5. X-ray crystallographic analysis of **1**

Suitable crystals were selected and mounted in thin-walled glass capillaries for X-ray structure analysis. The intensity data were collected at 294 K on a MSC/Rigaku RAXIS IIC imaging-plate diffractometer using graphite monochromated Mo–K α ($\lambda = 0.71073$ Å) radiation. Unit cell dimension was determined from four still frames, reflection data was collected by taking 45 oscillation frames in the range of 0–180°, $\Delta\psi = 4^\circ$, exposure 8 min per frame [28]. A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied by using the ABCOR program [29]. A summary of crystallographic data is given in Table 3.

The crystal structure was solved by the direct method, which yielded the positions of all non-hydrogen atoms. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a riding model. All computations were performed on an IBM compatible PC with the SHELX-97 package [30].

3.6. X-ray crystallographic analysis of **3**

Reflections were collected at 296 K on a Siemens P4 diffractometer using graphite monochromated Mo–K α ($\lambda = 0.71073$ Å) radiation. Unit cell parameters were determined from a least-square of the setting 29 reflections in the range $3.33 < \theta < 15.93^\circ$. During the course of collection of the intensity data no significant decays were observed. Data were corrected for Lorentz and polarization effects and empirical absorption. A total of 6367 data were collected of which 3462 with $F_o > 4\sigma(F_o)$ were subsequently used in the structure analysis. A summary of crystallographic data is given in Table 3.

The crystal structures were solved by direct methods and successive Fourier syntheses gave the coordinates of all non-hydrogen atoms. Hydrogen atoms were included in calculated positions. All calculations were carried out using the SHELX-97 program [30].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC nos. 136603 for complex **1** and 136604 for complex **3**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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